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SPECTROPHOTOMETRIC DETERMINATION OF DYSPROSIUM, HOLMIUM, ERBIUM, THULIUM, AND YTTERBIUM

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ABSTRACT

The transmittancies of solutions of the nitrates of dysprosium, holmium, erbium, thulium, and ytterbium were measured, over the range 350 to 1,000 $m\mu$, by means of a double-monochromator photoelectric spectrophotometer. Terbium and yttrium show no appreciable absorption in this range. The bands found most suitable for determination of the five elements are: for dysprosium, at 910 $m\mu$; for holmium, at 643 $m\mu$; for erbium, at 521 $m\mu$ and 653 $m\mu$; for thulium, at 684 $m\mu$; and for ytterbium, at 950 $m\mu$ and 973 $m\mu$.

Measurements were also made of the variation with concentration of the transmittancies of solutions of the nitrates of the five elements at the wavelengths given. The results obtained were applied to the analysis of several mixtures of rare earth oxides. The procedure supplements a similar one, previously published, for the analysis of mixtures of rare earths of the cerium group.

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I. INTRODUCTION

Few methods are available for the analysis of mixtures of the rare earth elements terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutecium, and yttrium, which are designated as the yttrium group. The fact that the members of this group vary in their magnetic susceptibility has been made use of by Urbain.¹ This method, however, is applicable only to mixtures of the diamagnetic yttrium with but one other element. Another method, also applicable only to binary mixtures containing yttrium, is based on determinations of the equivalent atomic weight.

The success achieved in the spectrophotometric determination of several members of the cerium group² of rare earth elements led to a similar investigation of the yttrium group. In the work reported in the present paper, a photoelectric spectrophotometer was used to

¹ G. Urbain, *Compt. rend.* **150**, 913 (1910).

² Clement J. Rodden, *Spectrophotometric determination of praseodymium, neodymium, and samarium*, J. Research NBS **26**, 557 (1941) RP1395.

obtain spectral transmittancy curves of solutions of the nitrates of terbium, dysprosium, holmium, erbium, thulium, ytterbium, and yttrium, and transmittancy-concentration curves for all of these except terbium and yttrium, which show no appreciable absorption. From these measurements it was found possible to determine dysprosium, holmium, erbium, thulium, and ytterbium in mixtures of these elements.

II. EXPERIMENTAL PART

1. APPARATUS

A Coleman double-monochromator photoelectric spectrophotometer, model 10 S, was used. The instrument was equipped with a slit stated by the manufacturer to select a spectral region of 5 μ . Square absorption cells 13.08 mm between faces and requiring 5 to 6 ml of solution were used.

In addition to the wavelength calibration from 400 to 750 m μ previously reported (*see footnote 2*), a glass containing erbium oxide² was used to obtain an additional calibration³ at 978 μ .

2. MATERIALS

Terbium.—The terbium oxide was obtained from the James collection of the late Charles James, of the University of New Hampshire. Its emission spectrum⁴ showed gadolinium as a major constituent. Dysprosium was present of the order of 0.1 percent. The color of the oxide was deep chocolate brown. An amount of the oxide (Tb_2O_3) equivalent to 0.25 g of terbium (plus gadolinium) was dissolved in nitric acid, and the solution evaporated to dryness on the steam bath. The residue was dissolved in water and diluted to 10 ml in a volumetric flask.

Dysprosium.—The dysprosium was obtained from the Eder collection.⁵ Its emission spectrum showed holmium and yttrium of the order of 0.01 percent each. The sample was converted to oxide, and a solution containing 0.025 g of dysprosium per milliliter was prepared as described under terbium. Other solutions of dysprosium were made by diluting this solution.

Holmium.—The holmium was obtained from the Eder collection. Its emission spectrum showed 1 to 10 percent of dysprosium and about 0.1 percent of yttrium and 0.01 percent of erbium. Transmittancy measurements showed the dysprosium content to be about 2 percent. The sample was converted to oxide, and a solution containing 0.019 g of holmium per milliliter was prepared as described under terbium.

Erbium.—The erbium was obtained from the Eder collection. Its emission spectrum showed thulium of the order of 2 percent, and about 0.1 percent each of holmium and yttrium.⁶ Transmittancy measurements gave approximately the same amount of thulium. The sample was converted to oxide and a solution containing 0.0245 g of erbium per milliliter was prepared as described under terbium.

³ Acknowledgment is made to R. Stair and B. F. Scribner, of this Bureau, for the transmission measurements on this glass.

⁴ Acknowledgment is made to B. F. Scribner and H. R. Mullin, of this Bureau, for the emission spectrum analyses.

⁵ The author wishes to thank W. F. Meggers, of this Bureau, for placing at his disposal samples of dysprosium, holmium, and erbium from the J. M. Eder collection of rare earth salts.

⁶ The spectrographic determination of thulium was made by comparison with samples of lanthanum nitrate containing known amounts of thulium.

Thulium.—The thulium oxide was obtained from the James collection. Its emission spectrum showed approximately 14 percent of ytterbium, and erbium and yttrium of the order of 0.01 percent each. Transmittancy measurements showed 15.5 percent of ytterbium. A solution containing 0.0185 g of thulium per milliliter was prepared as described under terbium.

Ytterbium.—The ytterbium oxide was obtained from the James collection. Its emission spectrum showed about 0.1 percent of lutecium and 0.01 percent of thulium. A solution of 0.025 g of ytterbium per milliliter was prepared as described under terbium.

Yttrium.—The yttrium oxide was obtained from the James collection. Its emission spectrum showed no rare earths. A solution containing 0.025 g of yttrium per milliliter was prepared as described under terbium.

It will be noted that the purity of some of the elements mentioned was determined by spectrochemical methods. Fortunately, ytterbium of high purity was available. Therefore the amount of ytterbium in the thulium could be determined. Then, from the data on the purity of the thulium, the amount of thulium in the erbium was obtained. The amount of gadolinium in the terbium is not known, but neither element has usable absorption bands. The absence of significant amounts of erbium in the holmium was also helpful. The amount of dysprosium in the holmium could be determined because high-purity dysprosium was available.

3. TRANSMITTANCY MEASUREMENTS

Spectral transmittancy curves for terbium, dysprosium, holmium, erbium, thulium, ytterbium, and yttrium nitrate solutions are shown in figures 1 to 7.⁷ For all but yttrium, readings were made at intervals of 10 $m\mu$, except where intense absorption bands occurred, in which case 1- to 2- $m\mu$ steps were used in order to obtain the transmittancy and wavelength at minimum transmittancy. Readings for yttrium were made at the wavelengths indicated in figure 7. Terbium and yttrium have no bands which can be used for their determination.⁸

Dysprosium has two bands that can be used for its determination, one at 808 $m\mu$ and another at 910 $m\mu$. The band at 910 $m\mu$ absorbs more strongly than the one at 808 $m\mu$, and in general is less affected by other elements of the yttrium group and is therefore to be preferred for the determination of dysprosium.

Holmium has three bands, one at 452 $m\mu$, one at 539 $m\mu$, and one at 643 $m\mu$. The absorption of the three bands is about the same. The band at 643 $m\mu$ is affected least by the other members of this group and is therefore to be preferred for the determination of holmium. Erbium has an appreciable effect which must be considered and corrected for by using the appropriate transmittancy-concentration curve.

Erbium has four bands, namely, those at 489 $m\mu$, at 521 $m\mu$, at 653 $m\mu$, and at 976 $m\mu$ in addition to a band at 381 $m\mu$. The latter band cannot be used readily because all of the solutions show an absorption in this region (see footnote 2). The absorption differs considerably

⁷ The transmittancy is defined as the ratio of the transmission of a cell containing solution to that of an identical cell containing distilled water.

⁸ As terbium is the only element of the yttrium group which forms a higher oxide, there is a possibility of reducing the Tb_4O_7 to Tb_2O_3 in a current of hydrogen and calculating the terbium content from the weight of water formed. However, it has not been established whether terbium occurs as Tb_4O_7 in mixtures with other rare earth oxides.

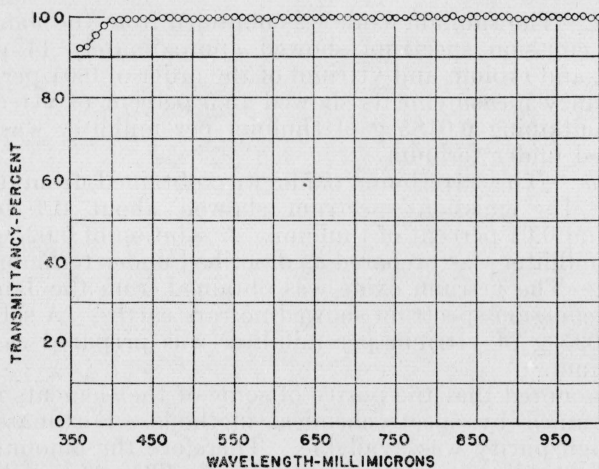


FIGURE 1.—Spectral transmittancy curve of terbium-gadolinium nitrate solution containing 0.25 g of terbium per 10 ml.

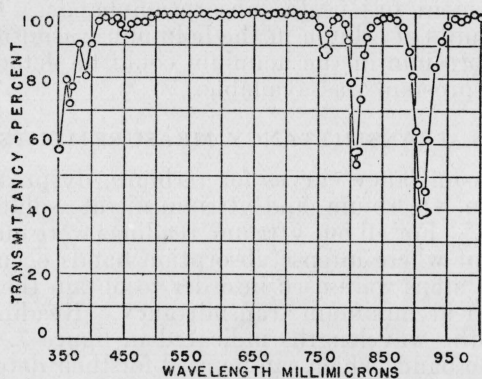


FIGURE 2.—Spectral transmittancy curve of dysprosium nitrate solution containing 0.25 g of dysprosium per 10 ml.

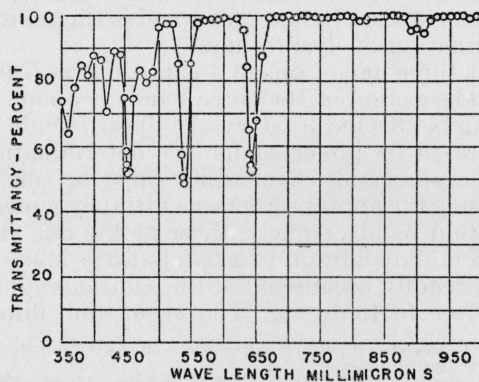


FIGURE 3.—Spectral transmittancy curve of holmium nitrate solution containing 0.19 g of holmium per 10 ml.

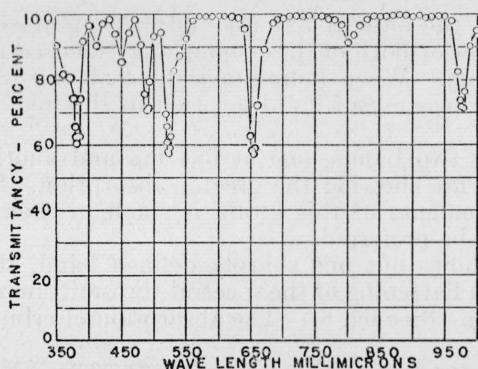


FIGURE 4.—Spectral transmittancy curve of erbium nitrate solution containing 0.245 g of erbium per 10 ml.

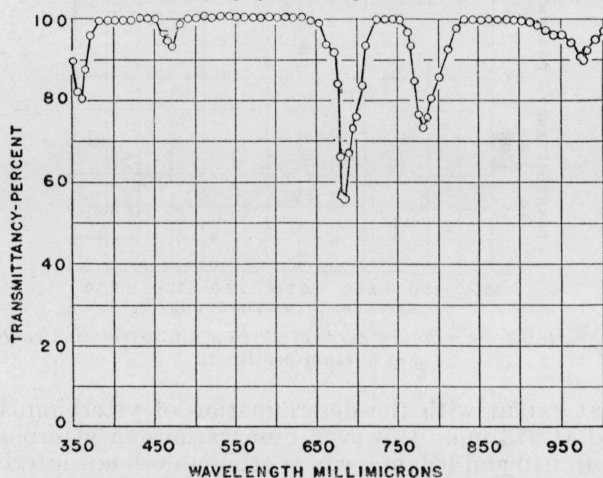


FIGURE 5.—Spectral transmittancy curve of thulium nitrate solution containing 0.185 g of thulium per 10 ml. Contains 15.5 percent of ytterbium.

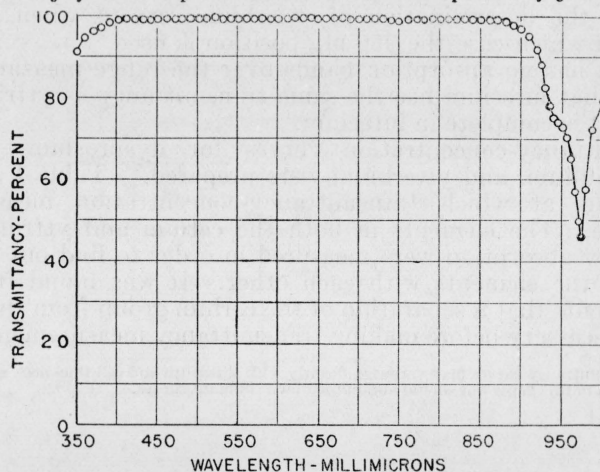


FIGURE 6.—Spectral transmittancy curve of ytterbium nitrate solution containing 0.25 g of ytterbium per 10 ml.

in these bands, the ones at $521\text{ m}\mu$ and $653\text{ m}\mu$ absorbing the more strongly. Either or both of these bands may be used for the determination of erbium. When holmium is present the band at $653\text{ m}\mu$ cannot be used because of its absorption in this region, as shown in figure 16.

Thulium has two bands, one at $684\text{ m}\mu$ and another at $780\text{ m}\mu$, the one at $684\text{ m}\mu$ showing the greater absorption. Since the effect of the other elements of this group is small in each band, the one at $684\text{ m}\mu$ is to be preferred.

Ytterbium shows but one sharply defined band, that at $973\text{ m}\mu$, but does show a flattening of the spectral transmittancy curve between 940 and $950\text{ m}\mu$. (See fig. 6.) The absorption of erbium interferes to

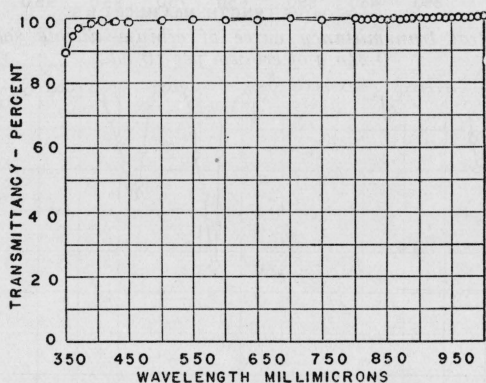


FIGURE 7.—Spectral transmittancy curve of yttrium nitrate solution containing 50.2 g of yttrium per 10 ml.

a very great extent with the determination of ytterbium by means of the band at $973\text{ m}\mu$. However, observations on ytterbium can be made at both 940 and $950\text{ m}\mu$, where erbium does not interfere. The absorption at these wavelengths is considerably less than at $973\text{ m}\mu$ but is still usable. The peak of the band at $973\text{ m}\mu$ is to be preferred for the determination of ytterbium, except when erbium is present, in which case the $950\text{ m}\mu$ position is used.

Yttrium has no absorption bands over the range measured. It is probable that lutecium has the same transmittancy as yttrium, since the $4f$ orbit is complete in lutecium.

Transmittancy-concentration curves for dysprosium, holmium, erbium, thulium, and ytterbium were prepared.⁹ Table 1 shows the wavelengths at which transmittancy-concentration measurements were made. The elements in both the cerium and yttrium groups which show absorption were measured in order to find out the interference of the elements with each other. It was found from these measurements that a separation of the cerium group from the yttrium group is necessary before making transmittancy measurements.

⁹ As the transmittancy curves may vary significantly with slit-width and cell thickness, analysts should not use the data in this paper but should obtain their own standard curves.

TABLE 1.—Wavelengths at which transmittancy-concentration measurements were made

Element	Wavelength	Element	Wavelength
	<i>mμ</i>		<i>mμ</i>
Sm.....	402	Er.....	653
Pr.....	446	Tm.....	684
Ho.....	452	Nd.....	742
Pr.....	469	Tm.....	780
Sm.....	479	Nd.....	798
Er.....	489	Dy.....	808
Er.....	521	Dy.....	910
Nd.....	521	Yb.....	940
Ho.....	539	Sm.....	950
Nd.....	578	Yb.....	950
Pr.....	589	Yb.....	973
Ho.....	643	Er.....	976

* Interferences in these absorption bands are avoided by a preliminary separation as double sodium sulfate.

The transmittancies of dysprosium nitrate solutions were obtained at 808 and 910 $m\mu$, with concentrations ranging from 0.0125 to 0.25 g of dysprosium per 10 ml. The results are shown in figure 8. Beer's law holds for both bands in the concentrations examined. Transmittancy-concentration curves of other elements of the yttrium group at 910 $m\mu$ are shown in figure 13.

The transmittancies of holmium nitrate solutions were obtained at 452, 539, and 643 $m\mu$, with concentrations varying from 0.0125 to 0.190 g of holmium per 10 ml. The results are shown in figure 9. There appears to be a slight variation from Beer's law for the bands at 452 and 539 $m\mu$. There is, however, no deviation from this law for the band at 643 $m\mu$. Transmittancy-concentration curves of other elements of the yttrium group at 643 $m\mu$ are shown in figure 14.

The transmittancies of erbium nitrate solutions were obtained at 489, 521, 653, and 976 $m\mu$, with concentrations varying from 0.020 to 0.245 g of erbium per 10 ml. The results are shown in figure 10. Beer's law holds for all the bands in the concentrations examined. Transmittancy-concentration curves of other elements of the yttrium group at 521 and 653 $m\mu$ are shown in figures 15 and 16, respectively.

The transmittancies of thulium nitrate solutions were obtained at 684 and 780 $m\mu$, with concentrations varying from 0.025 to 0.185 g of thulium per 10 ml. The results are shown in figure 11. Beer's law holds for both bands at the concentrations measured. Transmittancy-concentration curves of other elements of the yttrium group at 684 $m\mu$ are shown in figure 17.

The transmittancies of ytterbium nitrate solutions were obtained at 940, 950, and 973 $m\mu$, with concentrations varying from 0.020 to 0.25 g of ytterbium per 10 ml. The results are shown in figure 12. Beer's law holds for the three bands at the concentrations measured. Transmittancy-concentration curves of other elements of the yttrium group at 950 and 973 $m\mu$ are given in figures 18 and 19, respectively.

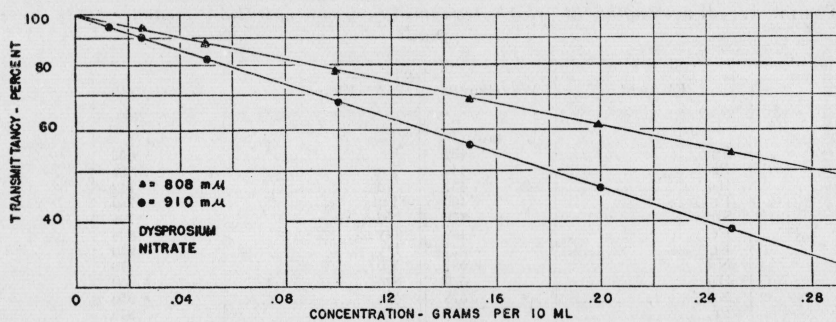


FIGURE 8.—*Transmittancy-concentration curves of dysprosium nitrate solutions.*
The concentration is expressed in terms of the element.

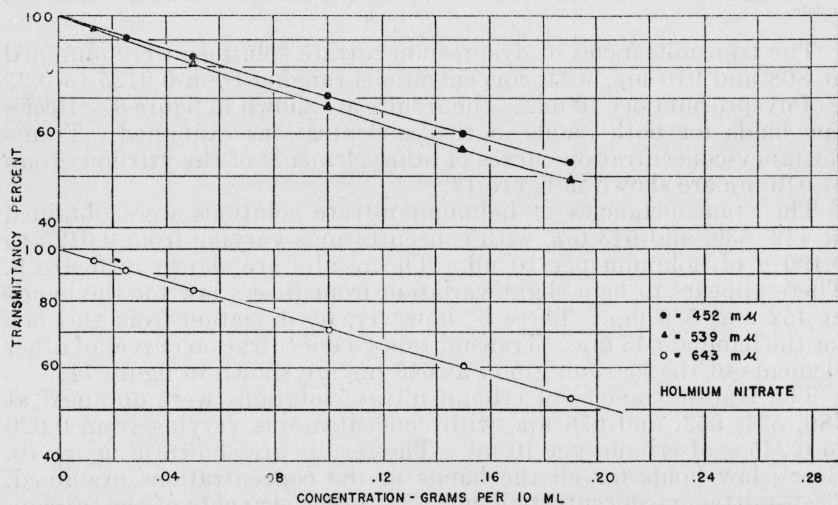


FIGURE 9.—*Transmittancy-concentration curves of holmium nitrate solutions.*
The concentration is expressed in terms of the element.

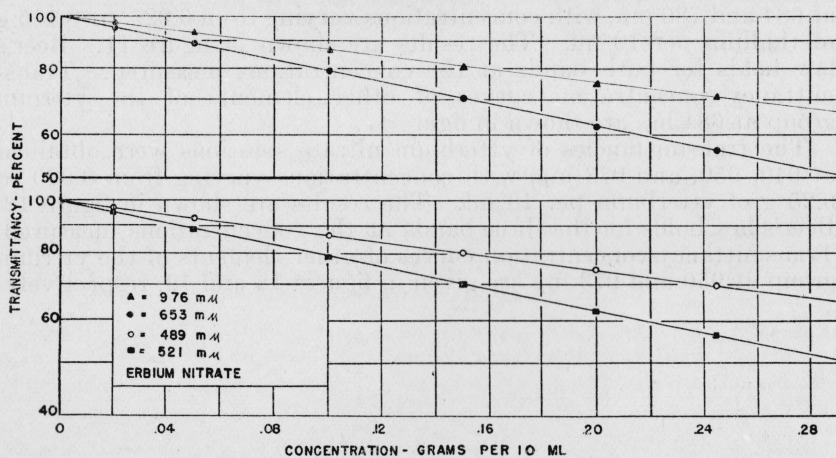


FIGURE 10.—*Transmittancy-concentration curves of erbium nitrate solutions.*
The concentration is expressed in terms of the element.

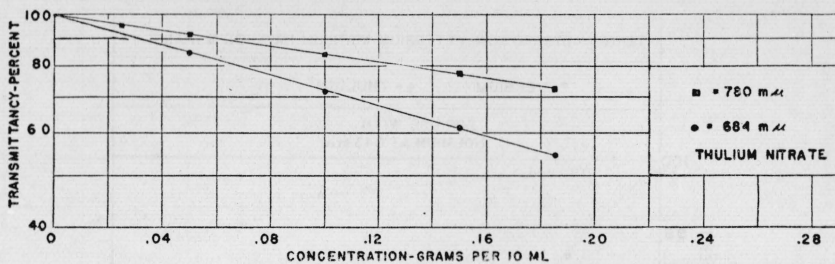


FIGURE 11.—Transmittancy-concentration curves of thulium nitrate solutions.

The concentration is expressed in terms of the element.

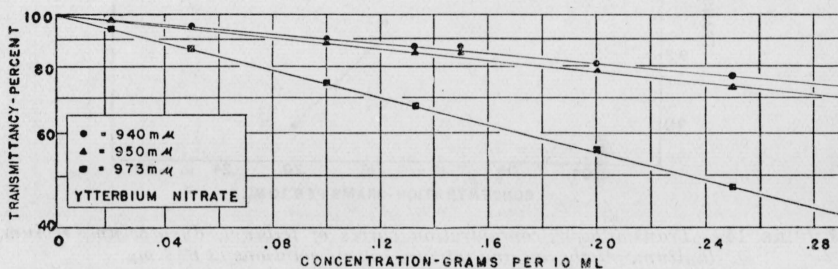


FIGURE 12.—Transmittancy-concentration curves of ytterbium nitrate solutions.

The concentration is expressed in terms of the element.

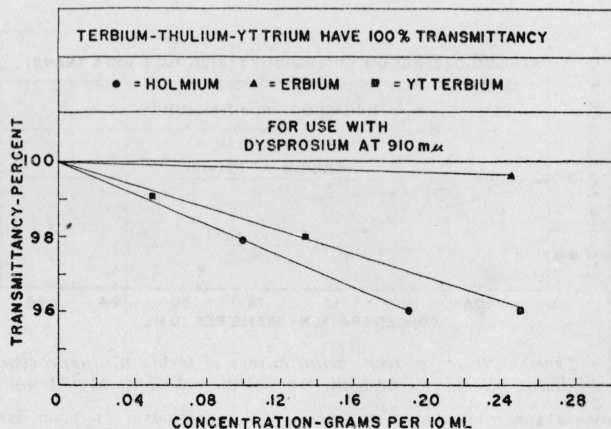


FIGURE 13.—Transmittancy-concentration curves of terbium, holmium, erbium, thulium, ytterbium, and yttrium nitrate solutions at 910 mμ.

The concentration is expressed in terms of the element. The concentration of terbium, thulium, yttrium is approximately 0.2 g of the element per 10 ml.

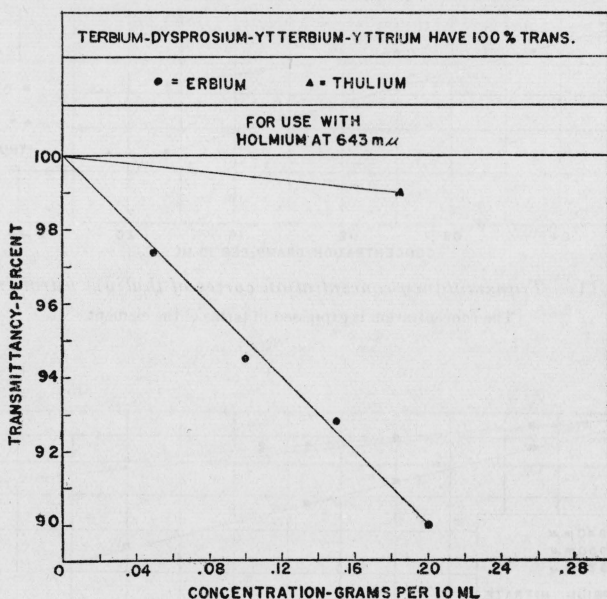


FIGURE 14.—Transmittancy-concentration curves of terbium, dysprosium, erbium, thulium, ytterbium, and yttrium nitrate solutions at 643 mμ.

The concentration is expressed in terms of the element. The concentration of terbium, dysprosium, ytterbium, yttrium is approximately 0.2 g of the element per 10 ml.

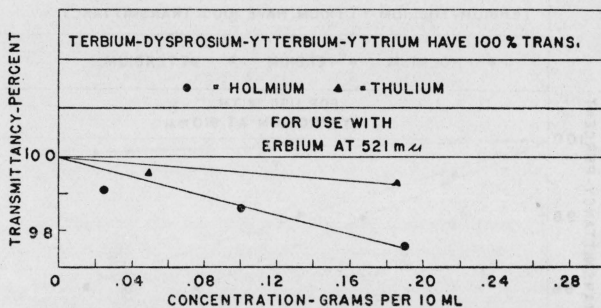


FIGURE 15.—Transmittancy-concentration curves of terbium, dysprosium, holmium, thulium, ytterbium, and yttrium nitrate solutions at 521 mμ.

The concentration is expressed in terms of the element. The concentration of terbium, dysprosium, ytterbium, yttrium is approximately 0.2 g of the element per 10 ml.

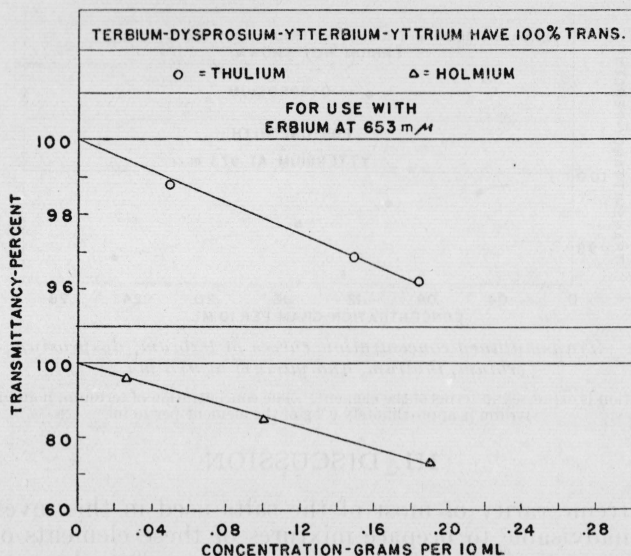


FIGURE 16.—Transmittancy-concentration curves of terbium, dysprosium, holmium, thulium, ytterbium, and yttrium at 653 mμ.

The concentration is expressed in terms of the element. The concentration of terbium, dysprosium, ytterbium, yttrium is approximately 0.2 g of the element per 10 ml.

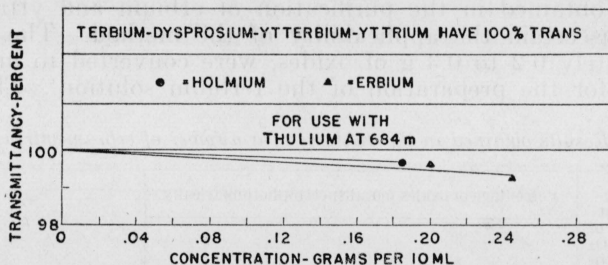


FIGURE 17.—Transmittancy-concentration curves of terbium, dysprosium, holmium, erbium, ytterbium, and yttrium nitrate solutions at 684 mμ.

The concentration is expressed in terms of the element. The concentration of terbium, dysprosium, ytterbium, yttrium is approximately 0.2 g of the element per 10 ml.

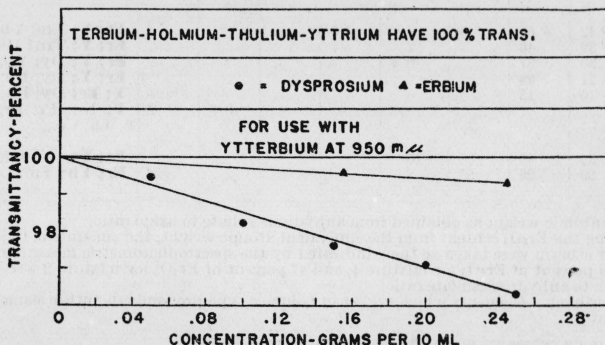


FIGURE 18.—Transmittancy-concentration curves of terbium, dysprosium, holmium, erbium, thulium, and yttrium at 950 mμ.

The concentration is expressed in terms of the element. The concentration of terbium, holmium, thulium, yttrium is approximately 0.2 g of the element per 10 ml.

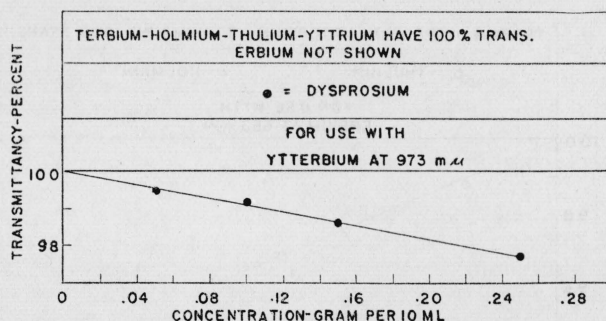


FIGURE 19.—*Transmittancy-concentration curves of terbium, dysprosium, holmium, erbium, thulium, and yttrium at 973 mμ.*

The concentration is expressed in terms of the element. The concentration of terbium, holmium, thulium-yttrium is approximately 0.2 g of the element per 10 ml.

III. DISCUSSION

The extreme rarity of most of the salts used in this investigation made it inadvisable to prepare mixtures of these elements of known composition. As the method had been shown¹⁰ to be satisfactory with known mixtures of members of the cerium group, it might be expected to be applicable to mixtures of the yttrium group elements.

An examination of certain fractions in the James collection which had been obtained in the purification of erbium and yttrium was made to ascertain the applicability of the method. The samples, approximately 0.2 to 0.3 g of oxides, were converted to nitrates as described for the preparation of the terbium solution. The trans-

TABLE 2.—*Results obtained in the analysis of a number of erbium-yttrium fractions*

Oxide mixture	Percentage of Er_2O_3 calculated from equivalent atomic weight ^a	Percentage of oxides found spectrophotometrically							Spectroscopic examination ^d
		Er_2O_3	Yb_2O_3	Tm_2O_3	Ho_2O_3	Dy_2O_3	Pr_2O_3	Nd_2O_3	
1-----	^b 42	50	3	3	0.5	-----	-----	-----	Er; Y; Tm; Yb; Dy; Ho.
2-----	^c 39	46	-----	2	.7	-----	-----	-----	Er; Y; Tm; Ho; Dy; Yb; Nd.
3-----	30	37	-----	0.4	-----	-----	-----	-----	Er; Y; Dy; Yb; Ho; Tm.
4-----	21	28	-----	-----	-----	-----	-----	-----	Er; Y; Dy; Ho; Tm; Yb.
5-----	10	13	-----	-----	-----	-----	-----	-----	Y; Er; Dy; Ho; Tm; Yb; Nd.
6-----	-----	-----	-----	-----	-----	-----	0.6	2	Y; Nd; Pr; Er; Dy; Ho; Yb; La; Ce.
7-----	39	40	36	10	-----	-----	-----	-----	Er; Yb; Y; Tm; Lu.
8-----	29	26	55	8	-----	-----	-----	-----	Er; Yb; Tm; Lu; Y.

^a Equivalent atomic weight as obtained from anhydrous sulfate to oxide ratio.

^b In calculating the Er_2O_3 content from the equivalent atomic weight, the amounts of the elements other than yttrium or erbium were taken as those indicated by the spectrophotometric measurements.

^c Values of 49 percent of Er_2O_3 for mixture 1, and 47 percent of Er_2O_3 for mixture 2 were obtained from hydrated sulfate to anhydrous sulfate ratio.

^d By B. F. Scribner. Elements which are set in boldface type predominate; other elements are present in minor amounts.

NOTE.—Where no values are given, the element was not detected.

¹⁰ Clement J. Rodden, *Spectrophotometric determination of praseodymium, neodymium, and samarium*, J. Research NBS **26**, 557 (1941) RP1395.

mittancies of the solutions were obtained at the wavelengths given in table 1 for the various elements, and the amount of each element was calculated as described for the determination of members of the cerium group (see footnote 10). Two samples from another fractionation series were also examined. The results are given in table 2 and are there compared with analyses based on equivalent atomic weights.

In some instances more than one band was used in determining an element in order to check the values obtained. For example, in a ytterbium-lutecium fraction the following values for ytterbium were obtained: 0.280 g at 940 $m\mu$; 0.280 g at 950 $m\mu$; and 0.281 g at 973 $m\mu$. In an erbium-yttrium fraction, 0.102 g of erbium was indicated at 489 $m\mu$, 0.101 g at 521 $m\mu$, and 0.100 g at 653 $m\mu$. A determination of thulium showed 0.024 g at 684 $m\mu$ and 0.024 g at 780 $m\mu$. The deviation from the true value in mixtures is unknown. With the cerium group mixtures, deviations greater than ± 3 mg are usually not obtained (see footnote 10). The same order probably holds for the yttrium group, as indicated in the results obtained for erbium at several wavelengths.

A commercial sample labeled "Guaranteed 95 percent thulia," obtained from a supply house, was examined and found to contain 78 percent of Yb_2O_3 , 12 percent of Er_2O_3 , and 8.7 percent of Tm_2O_3 .

The chief application of the method should be in following fractionations of yttrium group material. An important feature of this method for the analysis of rare earth compounds is that no material is lost during the course of the analysis. The method can also be used for the analysis of rare earth minerals. As outlined in the paper on the cerium group (see footnote 10), the rare earth elements are first separated from other elements, and the cerium and yttrium groups then separated by means of sodium sulfate. The cerium group elements—cerium, praseodymium, neodymium, samarium, and europium—can then be determined in the insoluble portion, and dysprosium, holmium, erbium, thulium, and ytterbium of the yttrium group elements in the soluble portion.

WASHINGTON, December 12, 1941.